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Magnetic behaviour of Co-Cr alloys above the critical concentration for ferromagnetism

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Abstract. — We have investigated Co-Cr alloys with chromium concentrations slightly larger than the critical concentration for long range magnetic order (25%). Our results suggest a strong inhomogeneous magnetic state consisting of clusters with a large distribution of formation temperatures. At low temperatures one observes a superparamagnetic to ferromagnetic transition followed by a ferromagnetic to spin glass transition at lower temperature in the range of concentration 25% to 29%.

1. Introduction. — Magnetization measurements performed on dilute Co-Cr alloys have shown that the variation $\Delta M/\Delta c$ of the average magnetic moment with the chromium concentration is as high as $-6.6 \mu_B$ [1, 2]. This and other physical properties [3, 4], have been interpreted as the occurrence of a virtual bound state above the Fermi level. However a recent calculation of the band structure of the Ni-Cr dilute alloy [5] shows that the density of states of the majority spin electrons on the impurity site not only consists of the virtual bound state but also extends over the whole d band of the matrix which lies below the Fermi level. Consequently the magnetic moment localized on the impurity site may be much smaller than $5 \mu_B$ and a large decrease of the average magnetic moment may also result from the decrease of the magnetization of the matrix. In fact NMR [6] and diffuse neutron scattering [7, 8] experiments suggest that the decrease of the magnetization mainly arises from the decrease of the magnetic moment of cobalt atoms which are nearest neighbours of the impurities, the magnetic moment of Cr atoms being smaller than $1 \mu_B$. This behaviour extends over alloys more concentrated in Cr until the long range magnetic order disappears near 25 at. % Cr. As the chromium solubility in h.c.p. cobalt is limited to 40% [9] the range of concentrations that we may investigate above the critical concentration is rather narrow and we only observed a typical giant moment behaviour without reaching a high enough concentration for the magnetic moments to collapse as in similar alloys such as CuNi [10, 11], VFe [12], NiV [13], and PdNi [14].

In the range of concentrations where the giant moments are observed, the temperature dependence of the low field magnetization evolves from typical ferromagnetic to spin glass like behaviour as the concentration in chromium increases. As an intermediate step the magnetization exhibits a plateau, the interpretation of which needs to be clarified from both theoretical and experimental points of view. A similar behaviour has been observed in Au-Fe concentrated alloys and different interpretations have been suggested [15, 16, 17, 18].

2. Experimental. — 2.1 Alloy preparation. — The alloys were prepared from 99.99% pure elements. Appropriate quantities of each constituent were melted
together in a water cooled copper boat in an induction furnace under He atmosphere. Each ingot was turned and melted five times and weight losses were such that concentrations are known within 0.1 at. % After melting, the alloys were homogenized at 1 000°C for 4 days under hydrogen atmosphere. Samples for magnetic investigations were shaped into spheres and the remaining parts of the ingots were cut and polished for X-rays and electron microprobe analysis. The entire samples were annealed at appropriate temperature under hydrogen atmosphere for 48 h before quenching into water in order to obtain the h.c.p. structure.

2.2 STRUCTURAL ANALYSIS. — An electron microprobe analysis of the samples revealed no significant segregation after the heat treatment and X-ray diffraction patterns only indicated a well resolved h.c.p. structure.

2.3 MAGNETIC MEASUREMENTS. — All measurements were performed using a vibrating sample magnetometer in fields up to 20 kOe and at temperatures in the range 2.5-300 K. Demagnetizing corrections were applied.

3. Discussion of the data. — We have investigated six specimens respectively containing 25, 26, 27.3, 28.2, 29.7 and 32.3 at. % Cr. We report in figure 1 the saturation magnetization \( \sigma_0 \) obtained from the Arrott plots at 4.2 K. We have reported figure 2 the temperature dependence of the magnetization in a small d.c. field applied at low temperatures for five specimens. For Co\(_{75}\)Cr\(_{25}\) the magnetization is «cut off» by the demagnetization factor at low temperatures. This is an indication of strong susceptibility but not necessarily of long range magnetic order [16]. The other specimens exhibit a quasi plateau between a higher temperature \( T_C \) and a lower temperature \( T_F \) where the magnetization decreases abruptly to lower values. We observe figure 4 that \( T_C \) and \( T_F \) tend, on increasing the concentration, to a unique value when a unique maximum of the susceptibility is observed. The field cooled magnetization (dashed line figure 2) which is often interpreted as the equilibrium response departs slightly from the zero field cooled magnetization at temperature much higher than \( T_C \) but it increases smoothly on decreasing the temperature below \( T_C \) and \( T_F \). The same field cooled data are shown (Fig. 3) in a \( \chi^{-1} \) vs. \( T \) plot. We observe on the data relative to the 28.2 % and to the 29.3 % that deviations from the Curie Weiss high temperature regime are already observed at a temperature \( T_S \) much higher than \( T_C \) (see Fig. 4).

From the general trend of the concentration dependence of \( T_S \) for two concentrations it may be

![Fig. 1. — Saturation magnetization \( \sigma_0 \) versus alloys concentration.](image)

![Fig. 2. — Magnetization versus temperature : — in a 30 Oe d.c. field for (a) 25, (b) 27.3, (c) 29.7 % at. Cr specimens; — in a 40 Oe d.c. field for (d) 26, (e) 28.2 % at. Cr specimens. The full line corresponds to increasing temperatures after cooling in zero field, and the dashed line to decreasing temperatures in the field.](image)
Fig. 3. — Reciprocal susceptibilities versus temperature. Black dots: cooled in the field. Light dots: cooled in a zero field. The dashed lines correspond to the high temperature Curie Weiss behaviour.

inferred (Fig. 4) that the high temperature paramagnetic Curie Weiss regime is out of reach in our measurement range for the alloys of lower concentration in Cr. The paramagnetic Curie constant in the high temperature Curie Weiss regime does not seem inconsistent with what would be expected for the Cr and Co present with the usual values of their magnetic moment. The average effective spin taken from the data is near 2. On decreasing $T$ below $T_g$ the observed susceptibility variation may be interpreted as traducing the formation of large superparamagnetic clusters. We tentatively estimated their magnitude $\mu$ and their number $N$ by comparing the
Table I. — Bulk magnetization $\sigma_0$, Curie constant $C$, effective magnetic moment $\mu_{\text{eff}}$, number $N$ of clusters and superparamagnetic asymptotic Curie temperature $\theta_p$ for four specimens.

<table>
<thead>
<tr>
<th>at. % Cr</th>
<th>$\sigma_0$ (emu. g$^{-1}$)</th>
<th>$C$ (emu. g$^{-1}$ Oe$^{-1}$. deg)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\theta_p$ (K)</th>
<th>$10^{-18}$ N/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.3</td>
<td>10.6</td>
<td>0.124</td>
<td>520</td>
<td>45</td>
<td>2.2</td>
</tr>
<tr>
<td>28.2</td>
<td>9.05</td>
<td>0.156</td>
<td>770</td>
<td>44</td>
<td>1.3</td>
</tr>
<tr>
<td>29.7</td>
<td>5.6</td>
<td>0.070</td>
<td>560</td>
<td>11</td>
<td>1.1</td>
</tr>
<tr>
<td>32.3</td>
<td>0.9</td>
<td>0.017</td>
<td>840</td>
<td>-10</td>
<td>0.1</td>
</tr>
</tbody>
</table>

superparamagnetic Curie constant in the superparamagnetic regime just above $T_c$ with the saturation magnetization $\sigma_0$ measured at low temperature using the approximate expression:

$$C \approx N\mu_{\text{eff}}^2/3k$$
$$\sigma_0 \approx N\mu_{\text{eff}}.$$

The data are reported in table I.

If the effective magnetic moment of the clusters is nearly concentration independent the number of clusters sharply decreases as the chromium concentration increases.

4. Interpretation of the data. — The essential results of our investigation are condensed in the phase diagram of figure 4.

$T_c$ is interpreted as the Curie temperature when the large clusters which are formed essentially around $T_s$, ferromagnetically order. The lower temperature $T_F$ is then the ferromagnetic to spin glass transition predicted by several theoretical models [19, 20, 21, 22] in the presence of a large ferromagnetic component of the interaction. The existence of such ferromagnetic correlations is attested by the fact that the superparamagnetic Curie temperature $\theta_p$ is positive (table I). On increasing the concentration we have directly a transition from superparamagnetism to the spin glass regime for concentrations larger than 29%. Notice that $\theta_p$ changes from positive to negative values between 29.7% and 32% Cr concentration.

This interpretation is made by analogy with similar interpretations which have been made on other systems [23, 24, 25, 26, 27, 28] and in particular in AuFe [17, 18] which exhibit essentially the same data.

The fact that the field cooled and the reversible susceptibilities are already different at temperatures much higher than $T_c$ is not necessarily a flaw for such an interpretation since the occurrence of remanence can be already justified in the frame of a superparamagnetic picture. There is anyway a large increase in the difference between field cooled and reversible susceptibility occurring at both temperatures $T_c$ and $T_F$ which still confirms the hypothesis of a phase transition occurring at those two points.

5. Conclusion. — We have determined the phase diagram (Fig. 4) of the magnetic transitions occurring in CoCr in the concentration range immediately above the concentration $c \approx 25$% Cr where long range ferromagnetism disappears. We conclude that there is a transition from superparamagnetic to ferro and then to spin glass order in the range $25 \% < c < 29 \%$ and a direct transition from superparamagnetic to spin glass order above this concentration. However the particular mechanism which governs the formation of the superparamagnetic clusters in this system is still only partially understood and probably more complicated in CoCr than it is in CuNi or AuFe.

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